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## (54) WASHING AND/OR BLEACHING COMPOSITIONS CONTAINING SILICATE CATION EXCHANGERS

(71) We, HENKEL & CIE. GMBH. a German Company, of 67 Henkelstrasse, Duesseldorf-Holthausen 4000, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to washing and/or bleaching compositions.

It is known that washing and cleaning compositions used in the household, in professional and trade laundries and in industrial plants, frequently contain relatively large amounts of condensed phosphates, especially tripolyphosphate, which is substantially responsible for the good cleaning action of these compositions. The phosphate content thereof has been criticised in publications concerning the protection of the environment; the view is often held that this phosphate which arrives in rivers and lakes by way of the waste water increases nutritive properties of the water, i.e. increases the growth of algae and therefore the consumption of oxygen. Attempts have therefore been made to eliminate the phosphate from washing and cleaning processes or from the agents used therefor or substantially to reduce its proportion therein.

It is already known from the German Specification No. 1,617,058 to use water-insoluble cellulose derivatives, especially phosphorylated cotton, in the washing process for softening the water. This proposal, however, does not provide a technically useful solution of the problem, since much too large amounts of phosphorylated cotton have to be added in order to bind the substances causing hardness of the water, quite irrespective of cellulose derivatives with smaller calcium binding capacities as, for example, sulphetyoxycellulose, carboxymethyl-cellulose and the succinic acid half ester of cellulose.

It is also known from the German Specification No. 2,055,423 to add to the pulverulent granular washing and cleaning compositions cation-exchanging cross-linked polymers insoluble in water and in alkaline solutions, as for example a cross-linked polymer from divinylbenzene and polyacrylic acid or poly-methacrylic acid. If these water-insoluble cation-exchangers present in the form of fine particles are added to the washing water, each is distributed in the textiles to be washed and can only be partially washed out again. For these reasons it has also been proposed to add the granular polymers to the washing water sewn in permeable bags. However, the contact with the washing water and therefore the action of the polymers is thereby greatly restricted.

The invention relates to a process for the washing and/or bleaching of textiles by treatment with an aqueous liquor which contains in suspension a synthetically produced, finely divided, water-insoluble, crystalline aluminium or boron silicate cation exchanger having a calcium binding capacity as hereinafter defined of at least 50 mg CaO/g of anhydrous active substance (=AS), containing bound water, of the general formula

$(cat_{2/n}O)x$, $Me_2O_3$, $(SiO_2)y$

in which cat represents a cation of valency n exchangeable with calcium, x is a number from 0.7 to 1.5, Me represents boron or aluminium and y is a number from 0.8 to 6, preferably 1.3 to 4, said silicate cation exchanger being capable of binding the inorganic salts causing hardness in the water.

The expression "calcium binding capacity" is to be understood as being the value obtained by the following test:—

1 litre of an aqueous solution containing 0.594 g of $CaCl_2$ (=330 mg CaO/litre) and adjusted to a pH value of 10 with dilute NaOH is mixed with 1g of a boron or aluminium silicate (referred to AS). The suspension is vigorously stirred at a temperature of 22°C (±2°C) for 15 minutes after which time the aluminium silicate is immediately filtered off and the residual hardness x in mg CaO/litre of the filtrate is determined. The calcium binding capacity is then determined from the formula

calcium binding capacity=300-x.

The calcium binding capacity may reach values of 200 mg CaO/g AS and lies preferably in the range from 100 to 200 mg CaO/g AS.

If the above test for calcium binding capacity is carried out at higher temperatures than 22°C e.g. at 60°C the values formed are consistently higher than those formed for the standard test at 22°C. This fact distinguishes the boron or aluminium silicates from most of the soluble complex-forming substances previously proposed for use in washing agents.

Sodium is preferred as the cation; it may however also be replaced by lithium, potassium, ammonium or magnesium as well as by the cations of water-soluble organic bases, for example by those of primary, secondary or tertiary amines or alkylolamines with not more than 2 carbon atoms per alkyl residue or not more than 3 carbon atoms per alkylol residue.

These compounds are denoted as "aluminium silicates" in the following pages for the sake of simplicity. Sodium aluminium silicates are preferably used. All data for their preparation and use obviously apply also to the other compounds claimed.

The above-defined aluminium silicates can be prepared synthetically in a simple way, for example by reaction of water-soluble silicates with water-soluble aluminates in the presence of water. For this purpose, aqueous solutions of the starting materials may be mixed with one another or a component present in the solid state is reacted with the other components present as an aqueous solution. Also by mixing two components present in the solid state, the desired aluminium silicates are obtained in the presence of water. In addition, aluminium silicates can be prepared from $Al(OH)_3$, $Al_2O_3$ or $SiO_2$ by reaction with alkali metal silicate or aluminium solutions. Finally, such substances are also formed from the molten components, but on account of the necessarily high melting temperatures and the need to convert the melts into finely divided products, this process appears economically less interesting.

Of course the cation-exchanging aluminium silicates to be used according to the invention are formed only when special precipitation conditions are adhered to, since otherwise products are formed which have no, or an insufficient, cation-exchanging capacity. The preparation of aluminium silicates utilisable according to the invention is described in the experimental part.

The aluminium silicates prepared by precipitation or by other processes and converted into a finely divided state in aqueous suspension are converted from the X-ray amorphous state into the crystalline state by heating at temperatures from 50° to 200°C. The preferred calcium binding capacity lying in the range from 100 to 200 mg CaO/g AS is found chiefly in compounds of the formula:

$$0.7—1.1\ Na_2O,\ Al_2O_3,\ 1.3—3.3\ SiO_2$$

This combined formula includes two types of different crystal structures (and/or their non-crystalline pre-products), which are also differentiated by their combined formulae. They are:

(a) $0.7—1.1\ Na_2O,\ Al_2O_3,\ 1.3—2.4\ SiO_2$
(b) $0.7—1.1\ Na_2O,\ Al_2O,\ >2.4—3.3\ SiO_2$

The different crystal structures are shown in the X-ray diffraction diagram; the d-values thereby found are given further below in the description of the preparation of the aluminium silicates.

The crystalline aluminium silicate present in aqueous suspension can be separated by filtration of the remaining aqueous solution and drying at temperatures of, for example, 50° to 800°C. The product contains more or less bound water, depending on the drying conditions. Anhydrous products are obtained at 800°C. If the water is to be completely driven off, this is possible by heating for an hour at 800°C.; in this way the AS contents of the aluminium silicates are also determined.

Such high drying temperatures are not advisable in the case of the aluminium silicates to be used in the invention; the temperature suitably does not exceed 400°C. It is a special advantage that products dried even at substantially lower temperatures of, for example, 80° to 200°C. up to the removal of the adhering liquid water are useful for the purposes of the invention. The aluminium silicates containing varying amounts of bound water thus prepared are obtained as a fine powder after the splitting up of the dried filter cake, of which the primary particle size is not more than 0.1 mm, but is mostly substantially lower and goes to the fineness of dust, for example, up to 0.1 $\mu$. In this case it is to be borne in mind that the primary particles may be all agglomerated to larger structures. In some processes of preparation primary particle sizes in the region of 50 to 1 $\mu$ are obtained.

Aluminium silicates 80% of which consists of particles of a size from 10 to 0.01 $\mu$, preferably from 8 to 0.1 $\mu$, are used with particular advantage. These aluminium silicates preferably contain no primary or secondary particles above 40 $\mu$. When such crystalline products are concerned, these are denoted as "microcrystalline" for the sake of simplicity.

The precipitation conditions may contribute to the formation of small particle sizes, while the aluminate and silicate solutions admixed with one another (which may also be simultaneously passed into the reaction vessel) are exposed to strong shearing stresses. When the crystalline aluminium silicates preferably used are prepared, the construction of large, possibly pervasive crystals is prevented by slow stirring of the crystallising mass.

Nevertheless, an undesired agglomeration of crystalline particles may occur on drying, so that it is advisable to remove these secondary particles in a suitable way, for example by air separation. Aluminium silicates obtained in a relatively coarse state, which have been ground to the desired grain size, can also be used. Suitable for this purpose are, for example, mills and/or air separators or combinations thereof. The latter are described, for example, by Ullmann: "Encyclopaedia of Technical Chemistry," Vo. 1, 1951, pages 632—634.

From the sodium aluminium silicates the aluminium silicates of other cations, for example those of potassium, magnesium or water-soluble organic bases, can be prepared in a simple way by base exchange. The use of these compounds instead of the sodium aluminium silicates may be suitable if a special effect is to be attained by loss of the said cations, for example, if the state of solution of surface-active compounds present in the wash composition is to be charged.

The amount of aluminium silicate required for obtaining a good washing or cleaning effect depends on the one hand on its calcium binding capacity, on the other hand on the amount and the degree of contamination of the materials to be treated and on the hardness and the amount of the water used. On use of hard water it is expedient to adjust the amount of aluminium silicate so that the residual hardness of the water does not amount to more than 5° German hardness (corresponding to 50 mg CaO/litre), preferably 0.5 to 2° German hardness (5 to 20 mg CaO/litre). To obtian an optimal washing or cleaning effect it is advisable, especially with very dirty substrates, to use an excess of aluminium silicates, in order to bind wholly or partly the substances causing the hardness contained in the detached contamination. Therefore the concentration of the aluminium silicates used may lie in the range of preferably 0.2 to 10 g AS/litre, especially 1 to 6 g AS/litre.

It was also found that the dirt can be removed substantially more quickly and/or more completely when an inorganic and/or organic builder is added to the treatment liquor which exerts a complex-forming and/or precipitating action on the calcium present as hardness producer in the water. As complex-forming builders for calcium, builders are also suitable for the purposes of the invention which have so small a compex-forming power that they have not previously been

regarded as typical complex-forming builders for calcium, but such compounds often have the ability to retard the precipitation of calcium carbonate from aqueous solutions.

Preferably small added amounts of, for example, 0.05 to 2 g/litre and especially 0.1 to 1 g/litre of complex-forming or precipitating builders for calcium are used, in order to accelerate appreciably and to improve the removal of the dirt. Substantially larger amounts may also be used, but when phosphorous-containing complex-forming or precipitating builders are used, amounts should be chosen so that the charge of phosphorous in the waste water is distinctly less than when the at present usual washing composition based on triphosphate is used.

Inorganic builders are, for example, pyrophosphates, triphosphates, higher polyphosphates and metaphosphates.

Organic builders are the polycarboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids, carboxyalkylethers, polyanionic polymers, especially the polymeric carboxylic acids and the phosphonic acids, these compounds being used mostly in the form of their water-sobluble salts.

Examples of polycarboxylic acids are dicarboxylic acids of the general formula $HOOC—(CH_2)_n—COOH$ with n=0 to 8, also maleic acid, methylenemalonic acid, citraconic acid, mesaconic acid, itaconic acid, non-cyclic polycarboxylic acids with at least 3 carboxyl groups in the molecule, as for example tricarballylic acid, aconitic acid, ethylenetetracarboxylic acid, 1,1,3,3-propanetetracarboxylic acid, 1,1,3,3,5,5-pentane-hexacarboxylic acid, hexanehexacarboxylic acid, cyclic di- or poly-carboxylic acids, as for example, cyclopentane-tetracarboxylic acid, cyclohexanehexacarboxylic acid, tetrahydrofuran-tetracarboxylic acid, phthalic acid, terephthalic acid, benzenetri-, tetra- or pentacarboxylic acid as well as mellitic acid.

Examples of hydroxymono- or hydroxy-poly-carboxylic acids are glycollic acid, lactic acid, malic acid, tartronic acid, methyltartronic acid, gluconic acid, glyceric acid, citric acid, tartaric acid and salicylic acid.

Examples of aminocarboxylic acids are glycine, glycylglycine, alanine, asparagine, glutamic acid, aminobenzoic acid, iminodi- or -tri-acetic acid, hydroxyethyl-iminodiacetic acid, ethylenediamino-tetraacetic acid, hydroxyethyl-ethylenediamino-triacetic acid, diethylenetriamino-pentaacetic acid as well as higher homologues, which may be prepared by polymerisation of an N-aziridylcarboxylic acid derivative, for example of acetic acid, succinic acid, tricarballylic acid, and subsequent saponification, or by condensation of polyamines with a molecular weight of 500 to 10,000 with chloroacetic acid or bromoacetic acid salts.

Examples of carboxyalkylethers are 2,2-hydroxydisuccinic acid and other etherpolycarboxylic acids, especially polycarboxylic acids containing carboxymethylether groups, to which belong corresponding derivatives of the following polyhydric alcohols or hydroxycarboxylic acids, which may be completely or partly etherified with glycollic acid: glycol, di- or tri-glycols, glycerine, di- or triglycerines, glycerinemonoethylether, 2,2-dihydroxymethylpropanol, 1,1,1-trihydroxymethyl-ethane, 1,1,1-trihydroxymethylpropane, erythritol, pentaerythritol, glycollic acid, lactic acid, tartronic acid, methyltartronic acid, glyceric acid, erythronic acid, malic acid, citric acid, tartaric acid, trihydroxyglutaric acid, saccharic acid and mucic acid.

As transition types of the polymeric carboxylic acids may be mentioned the carboxymethylethers of sugar, starch and cellulose.

Among the polymeric carboxylic acids, for example, the polymers of acrylic acid, hydroxyacrylic acid, maleic acid, itaconic acid, mesaconic acid, aconitic acid, methylenemalonic acid, citraconic acid and the like, the copolymers of the above mentioned carboxylic acids with one another or with ethylenically unsaturated compounds such as ethylene, propylene, isobutylene, vinyl alcohol, vinylmethylether, furan, acrolein, vinyl acetate, acrylamide, acrylonitrile, methacrylic acid, crotonic acid etc., as for example the 1:1 mixed polymers from maleic anhydride and ethylene or propylene or furan, play a special part.

Further polymeric carboxylic acids of the type of the polyhydroxypolycarboxylic acids or polyaldehydo-polycarboxylic acids are essentially substances built up from acrylic acid- and acrolein-units or acrylic acid- and vinyl alcohol-units, which are obtainable by copolymerisation of acrylic acid and acrolein or by polymerisation of acrolein and a subsequent cannizzaro reaction possibly in the presence of formaldehyde.

Examples of phosphorus-containing organic complex-forming substances are alkanepolyphosphonic acids, amino- and hydroxyalkanepolyphosphonic acids and

phosphonocarboxylic acids, as for example the compounds methanediphosphonic acid, propane-1,2,3-triphosphonic acid, butane-1,2,3,4-tetraphosphonic acid, polyvinylphosphonic acid, 1-aminoethane-1,1-diphosphonic acid, 1-amino-1-phenyl-1-diphosphonic acid, aminotrimethylene-triphosphonic acid, methylamino- or ethylaminodimethylenediphosphonic acid, ethylenediaminotetramethylenetetraphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, phosphonoacetic acid, phosphonopropionic acid, 1-phosphonoethane-1,2-dicarboxylic 2-phosphonopropane-2,3-dicarboxylic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 2-phosphonobutane-2,3,4-tricarboxylic acid as well as mixed polymers from vinylphosphonic acid and acrylic acid.

By the use of the above-described aluminium silicates according to the invention it is directly possible to keep the phosphorus content of the treatment baths at not more than 0.6 g/litre, preferably at not more than 0.3 g/litre of organically and/or inorganically bound phosphorus, even when phosphorus-containing inorganic or organic complex-forming or precipitating means for calcium are used. However, a good result can also be obtained on working without phosphorus.

The process according to the invention of washing and/or bleaching all types of textiles can be effected in industry, commercial laundries and in the home.

The textiles to be washed may consist of a wide variety of fibres of natural or synthetic origin. To these belong, for example, cotton, regenerated cellulose or linen as well as textiles which contain highly finished cotton or synthetic chemical fibres, as for example polyamide, polyester, polyacrylonitrile, polyurethane, polyvinyl chloride or polyvinylidene chloride fibres. The washing agents according to the invention can also be used for washing the textiles from synthetic fibres-cotton mixed fabrics known as "easy-care", and sometimes also as "non-iron".

In the washing and cleaning of such substrates with use of aqueous cleaning baths containing suspended aluminium silicates, the aqueous cleaning baths contain the usual constituents of such treatment baths. These include surface-active compounds, surface-active or non-surface-active foam stabilisers or inhibitors, textile softeners, chemically acting bleaching agents such as percompounds as well as stabilisers and/or activators for these, dirt carriers, corrosion inhibitors, antimicrobial substances, enzymes, brighteners, dyestuffs and perfumes and so on.

The above-mentioned substances may be present in washing and cleaning baths in the following concentrations:

0—2.5 g/litre surface-active substances
0—6 g/litre builders
0—0.4 g/litre active oxygen or equivalent amounts of active chlorine.

The pH value of the treatment baths may lie in the range from 6 to 13, preferably 8.5 to 12, depending on the substrate to be washed or cleaned.

For a relatively long time attempts have been made to find a useful substitute for phosphate, which is not only able to bind calcium, but can also be biologically decomposed in the waste water. Therefore a wide variety of organic compounds has been proposed as phosphate substitutes. The technical teaching according to the invention to use water-insoluble cation-exchanging aluminium silicates for this purpose is therefore a complete departure from the direction in which the whole technical world is working. It is therefore particularly surprising that the water-insoluble aluminium silicates are completely washed out of textiles. The use of the aluminium silicates causes in a double respect a discharge of the waste water the amounts of phosphorus arriving in the waste water are greatly reduced or wholly eliminated; moreover the aluminium silicates need no oxygen for the biological decomposition. They are of mineral nature, are deposited gradually in filter plants or in natural waters and consequently fulfil the ideal requirements for a phosphate substitute.

However, even during washing and bleaching they have also technical washing and cleaning advantages, compared with other already proposed phosphate substitutes; they adsorb coloured impurities and therefore reduce the cost of chemically acting bleaching agents.

For the carrying out of the claimed process, the invention also relates to certain compositions which contain calcium binding substances. Besides as least one washing and/or bleaching action, inorganic or organic compound, these compositions contain as calcium binding compound the above-defined aluminium silicates. Apart from this, other usual assistants and additives usually present in smaller amount, may be present in such means.

The content of aluminium silicate may lie within the range of 5 to 95, preferably 15 to 60%.

The compositions according to the invention may further contain complex-forming or precipitation builders for calcium, in quantities of 2 to 15%.

The amount of the inorganic phosphates and/or organic phosphorous compounds present in the compositions according to the invention should not be greater than corresponds to a total phosphorous content of the composition of 6%, preferably of 3%.

All these percentage data are weights per cent; they relate to the anhydrous active substance (=AS).

The compounds with a washing, bleaching or cleaning action contained in the compositions of the invention include, surface-active compounds, surface-active or non-surface-active foam stabilisers or inhibitors, textile softeners, neutral or alkaline reacting builder substances, chemically acting bleaching agents as well as stabilisers and/or activators for these. Other assistants and additives usually present in smaller amount are, corrosion inhibitors, anti-microbial substances, dirt carriers, enzymes, brighteners, dyestuffs and perfumes.

The composition of typical textile washing compositions to be used at temperatures in the range from 50° to 100°C. lies within the range of the following formulation:

(A) 5—30% of an anionic surfactant of the sulphonate or sulphate type and/or non-ionic and/or amphoteric surfactant.
(B) 5—70% of an aluminium silicate (referred to AS)
(C) 2—45% of a builder which is complex-forming and/or is a precipitant for calcium.
(D) 0—50% of an alkaline builder other than (C) above, and
(E) 0—50% of a bleaching agent and other conventional detergent additives.

Now follows an enumeration of the substances suitable for use in the compositions according to the invention.

The surface-active compounds contain in the molecule at least one hydrophobic organic residue and a water-solubilising anionic, amphoteric or non-ionic group. The hydrophobic residue is usually an aliphatic hydrocarbon residue having 8 to 26, preferably 10 to 22 and especially 12 to 18 carbon atoms or an alkylaromatic residue having 6 to 18, preferably 8 to 16 aliphatic carbon atoms.

Useful anionic surface-active compounds are, for example, soaps from natural or synthetic, preferably saturated fatty acids, possibly also from resin or naphthenic acids. Suitable synthetic anionic surface-active compounds are those of the sulphonate, sulphate and the synthetic carboxylate type.

Suitable surface-active compounds of the sulphonate type are alkylbenzenesulphonates ($C_{9-15}$-alkyl), mixtures of alkene- and hydroxyalkane-sulphonates, as well as disulphonates, such as are obtained, for example, from monoolefines with terminal or non-terminal double bond by sulphonation with gaseous sulphur trioxide and subsequent alkaline or acid hydrolysis of the sulphonation products. In addition alkanesulphonates, which are obtainable from alkanes by sulphochlorination or sulphoxidation and subsequent hydrolysis or neutralisation or by bisulphite addition to olefines, are suitable. Further useful surface-active compounds of the sulphonate type are the esters of $\alpha$-sulpho-fatty acids, for example the $\alpha$-sulphonic acids from hydrogenated methyl or ethyl esters of coconut, palm kernel or tallow fatty acid.

Suitable surface-active compounds of the sulphate type are the sulphuric acid monoesters of primary alcohols (for example from coconut fatty alcohols, tallow fatty alcohols or oleyl alcohol) and secondary alcohols thereof. In addition, sulphated fatty acid alkanolamides, fatty acid monoglycerides or reaction products of 1 to 4 mol of ethylene oxide with primary or secondary fatty alcohols or alkylphenols are suitable.

Further suitable anionic surface-active compounds are the fatty acid esters or amides of hydroxy- or amino-carboxylic acids or sulphonic acid, as for example, the fatty acid sarcosides, glycollates, lactates, taurides or isethionates.

The anionic surface-active compounds may be present in the form of their sodium, potassium and ammonium salts as well as soluble salts of organic bases, such as mono-, di- or tri-ethanolamine.

Useful non-ionic surface-active compounds are products of addition of 4 to 40, preferably 4 to 20 mol of ethylene oxide to 1 mol of fatty alcohol, alkylphenol, fatty acid, fatty amine, fatty acid amide or alkanesulphonamide. Of particular

importance are the products of addition of 5 to 16 mol of ethylene oxide to coconut or tallow fatty alcohols, oleyl alcohol or secondary alcohols with 8 to 18, preferably 12 to 18 carbon atoms, as well as to mono- or di-alkylphenols with 6 to 14 carbon atoms in the alkyl residues. Besides these water-soluble nonionics, however, water-insoluble or not completely water-soluble polyglycolethers with 1 to 4 ethyleneglycolether residues in the molecule are also of interest, especially when they are used together with water-soluble non-ionic or anionic surface-active compounds.

Furthermore the water-soluble products of addition, containing 20 to 250 ethyleneglycolether groups and 10 to 100 propyleneglycolether groups, of ethylene oxide to polypropyleneglycol (=Pluronics (Registered Trade Mark)), alkylenediaminopolypropylene glycol (=Tetronics (Registered Trade Mark)) and alkylpolypropyleneglycols with 1 to 10 carbon atoms in the alkyl chain are useful as nonionic surface-active compounds, in which the polypropyleneglycol chain functions as a hydrophobic residue.

Non-ionic surface-active compounds of the amine-oxide or sulphoxide type are also useful.

The foaming power of the surface-active compounds can be increased or reduced by combination of suitable surface-active compounds; a reduction can also be obtained by additions of non-surface-active organic substances.

Surface-active carboxy- or sulpho-betaines as well as the above-mentioned nonionics of the alkylolamide type are suitable as foam stabilisers, above all in the case of surface-active compounds of the sulphonate or sulphate type; moreover, fatty alcohols or higher terminal diols have been proposed for this purpose.

A reduced foaming power, which is desirable when working in machines, is frequently obtained by combination of different types of surface-active compounds, for example of sulphates and/or sulphonates with nonionics and/or with soaps. With soaps the foam inhibition rises with the degree of saturation and the carbon number of the fatty acid residue; soaps of the saturated $C_{20-24}$-fatty acids are therefore especially suitable as foam inhibitors.

The non-surface-active foam inhibitors include N-alkylated aminotriazines possibly containing chlorine, which are obtained by reacting 1 mol of cyanuric chloride with 2 to 3 mol of a mono- and/or di-alkylamine with 6 to 20, preferably 8 to 18 carbon atoms in the alkyl residue. Propoxylated and/or butoxylated aminotriazines have a similar action, for example products, which are obtained by addition of 5 to 10 mol of propylene oxide to 1 mol of melamine and further addition of 10 to 50 mol of butylene oxide to this propylene oxide derivative.

Also suitable as non-surface-active foam inhibitors are water-insoluble organic compounds such as paraffins or halogenated paraffins with melting points below 100°C., aliphatic $C_{18}$ to $C_{40}$ ketones as well as aliphatic carboxylic acid esters, which contain in the acid or in the alcohol residue, possibly also in each of these two residues, at least 18 carbon atoms (for example triglycerides or fatty acid-fatty alcohol esters); they can be used chiefly in combinations of surface-active compounds of the sulphate and/or sulphonate type with soaps for inhibiting the foam.

Particularly weakly foaming nonionics, which may be used both alone and in combination with anionic, amphoteric and non-ionic surface-active compounds and which reduce the foaming power of strongly foaming surface-active compounds, are the products of addition of propylene oxide to the already mentioned surface-active polyethyleneglycolethers as well as the likewise already described products of addition of ethylene oxide to polypropyleneglycols and alkylenediamino-polypropyleneglycols or to $C_{1-10}$-alkyl-polypropyleneglycols.

Suitable builder substances are weakly acid, neutral or alkaline reacting inorganic or organic salts.

Weakly acid, neutral or alkaline reacting salts utilisable according to the invention are, for example, the bicarbonates, carbonates, borates or silicates of the alkali metals, alkali metal sulphates as well as the alkali metal salts of organic, non-surface-active sulphonic acids, carboxylic acids and sulphocarboxylic acids containing 1 to 8 carbon atoms. These include, for example, water-soluble salts of benzene-, toluene- or xylene-sulphonic acid, water-soluble salts of sulphoacetic acid, sulphobenzoic acid or sulphodicarboxylic acids.

The components of the textile washing compositions according to the invention especially the builder substances, are usually chosen so that the compositions have a neutral to strongly alkaline reaction, so that the pH value of a 1% solution of the composition lies mostly in the range of 7 to 12. For

example, fine washing compositions usually have a neutral to weakly alkaline reaction (pH value=7 to 9.5), while steeping, prewashing and boiling washing compositions are adjusted so that they are more strongly alkaline (pH value=9.5—12, preferably 10—11.5). When higher pH values are needed for special cleaning purposes, these can be easily adjusted by use of alkali metal silicates with suitable $Na_2O:SiO_2$ ratios or caustic alkalis.

Among the compounds yielding $H_2O_2$ in water and serving as bleaching agents. sodium perborate-tetrahydrate ($NaBO_2,H_2O_2,3H_2O$) and the monohydrate ($NaBO_2,H_2O_2$) are of special importance. However, other $H_2O_2$-yielding borates are also utilisable, for example perborax $Na_2B_4O_7,4H_2O_2$. These compounds may be partly or completely replaced by other active oxygen carriers, especially by peroxyhydrates, such as peroxycarbonates ($Na_2CO_3$, $1.5H_2O_2$), peroxypyrophosphates, citrate perhydrates, urea-$H_2O_2$- or malamine-$H_2O_2$-compounds as well as peracid salts yielding $H_2O_2$, such as for example, salts of Caro's acid ($KHSO_5$), perbenzoates or peroxyphthalates.

It is advisable to incorporate the usual water-soluble and/or water-insoluble stabilisers for the peroxy-compounds together with these in amounts from 0.25 to 10% by weight. Suitable water-insoluble stabilisers, which for example, constitute 1 to 8, preferably 2 to 7% of the weight of the total preparation, are the magnesium silicates $MgO:SiO_2$=4:1 to 1:4, preferably 2:1 to 1:2 and especially 1:1, obtained usually by precipitation from aqueous solutions. Other alkaline earth metal, cadmium or tin silicates of corresponding compositions can be used in their place. Water-containing oxides of tin are also suitable as stabilisers. Water-soluble stabilisers which may be present together with water-insoluble, stabilisers are the organic complex-forming compounds, the amount of which may constitute 0.25 to 5, preferably 0.5 to 2.5% by weight of the total compositions.

In order to obtain a satisfactory bleaching action during the washing even at temperatures below 80°C., especially in the range from 60° to 40°C., activator-containing bleaching components are preferably incorporated in the compositions.

Serving as activators for percompounds yielding $H_2O_2$ in water are N-acyl- and O-acyl-compounds forming organic per-acids with this $H_2O_2$, especially acetyl-, propionyl- or benzoyl-compounds, as well as carbonic acid or pyrocarbonic acid esters. Useful compounds are among others: N-diacylated and N,N'-tetraacylated amines as for example, N,N,N',N'-tetraacetyl-methylenediamine or -ethylenediamine, N,N-diacetylaniline and N,N-diacetyl-p-toluidine or 1,3-diacylated hydantoins, alkyl-N-sulphonyl-carbonamides, for example N-methyl-N-mesyl-acetamide, N-methyl-N-mesyl-benzamide, N-methyl-N-mesyl-p-nitrobenzamide, and N-methyl-N-mesyl-p-methoxybenzamide, N-acylated cyclic hydrazides, acylated triazoles or urazoles as for example, the monoacetylmaleic acid hydrazide, O,N,N-trisubstituted hydroxylamines as for example O-benzoyl-N,N-succinyl-hydroxylamine, O-acetyl-N,N-succinyl-hydroxylamine, O-p-methoxybenzoyl-N,N-succinyl-hydroxylamine, O-p-nitrobenzoyl-N,N-succinyl-hydroxylamine and O,N,N-triacetyl-hydroxylamine, N,N'-diacyl-sulphurylamide, as for example N,N'-dimethyl-N,N'-diacetyl-sulphurylamide, and N,N'-diethyl-N,N'-dipropionyl-sulphurylamide, triacyl cyanurates, for example triacetyl- or tribenzoyl-cyanurate, carboxylic acid anhydrides, for example benzoic anhydride, m-chloro-benzoic anhydride, phthalic anhydride, 4-chlorophthalic anhydride, sugar esters, such as for example glucose penta-acetate, 1,3-diacyl-4,5-diacyloxy-imidazolidine, for example the compounds of 1,3-diformyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-diacetoxy-imidazolidine, 1,3-diacetyl-4,5-dipropionyloxy-imidazolidine, acylated glycolurils, as for example tetrapropionylglycoluril or diacetyl-dibenzoyl-glycoluril, diacylated 2,5-diketopiperazines, as for example 1,4-diacetyl-2,5-diketopiperazine, 1,4-dipropionyl-2,5-diketopiperazine, 1,4-di-propionyl,3,6-dimethyl-2,5-diketopiperazine, acetylation or benzoylation products of propylenediurea or 2,2-dimethyl-proplyenediurea (2,4,6,8-tetraaza-bicyclo-(3,3,1)-nonane-3,7-dione or its 9,9-dimethyl derivative), sodium salts of p-(ethoxycarbonyloxy)-benzoic acid and p-(propoxycarbonyloxy)-benzenesulphonic acid.

The active chlorine compounds serving as bleaching agents may be inorganic or organic.

The inorganic active chlorine compounds include alkali metal hypochlorites, which may be used especially in the form of their mixed salts or addition compounds to orthophosphates or to condensed phosphates as for example, to pyro- and poly-phosphates or to alkali metal silicates. When the washing agents

and washing assistants contain monopersulphates and chlorides, active chlorine is formed in aqueous solution.

Suitable organic active chlorine compounds are especially the N-chloro-compounds, in which one or two chlorine atoms are linked to a nitrogen atom, while the third valency of the nitrogen atoms preferably leads to a negative group, especially to a CO— or $SO_2$— group. Dichloro- and trichloro-cyanuric acid or their salts, chlorinated alkylguanides or alkylbiguanides, chlorinated hydantoins and chlorinated melamines belong to these compounds.

In addition, dirt carriers may be contained in the preparations of the invention which keep the dirt detached from the fibres suspended in the bath and thus prevent greying. Water-soluble colloids of usually organic nature are suitable for this purpose, as for example, the water-soluble salts of polymeric carboxylic acids, glue, gelatine, salts of ethercarboxylic acids or ethersulphonic acids of starch or cellulose or salts of acid sulphuric acid esters of cellulose or starch. Water-soluble polyamides containing acid groups are also suitable for this purpose. Furthermore, soluble starch preparations and starch products other than those mentioned above can be used, as for example degraded starch, aldehyde starches and so forth. Polyvinylpyrrolidone is also useful.

The enzyme preparations to be used are mostly a mixture of enzymes with different action, for example of proteases, carbohydrases, esterases, lipases, oxidoreductases, catalases, peroxidases, ureases, isomerases, lyases, transferases, desmolases or nucleases. The enzymes obtained from strains of bacteria or fungi such as Bacillus subtilis or Streptomyces griseus are of special interest, especially proteases or amylases, which are relatively stable towards alkali, percompounds and anionic surface-active compounds and are still active at temperatures up to 70°C.

Enzyme preparations are usually put on the market by the manufacturers as aqueous solutions of the active substances or as powders, granules or cold-sprayed products. The frequently contain as diluent or blending agent sodium sulphate, sodium chloride, alkali metal ortho-, pyro- or poly-phosphates, especially tripolyphosphate. Particular value is placed on dust-free preparations; they are obtained in known way by incorporation of oily or pasty nonionics or by granulation by means of melts of salts in their own water of crystallisation.

Enzymes may be incorporated which are specific for a particular type of dirt, for example proteases or amylases or lipases; combinations of enzymes of different action are preferably used, especially combinations of proteases and amylases.

As optical brighteners for cotton the washing agents may contain especially derivatives of diaminostilbenedisulphonic acid or their alkali metal salts. For example, salts of 4,4'-bis (2-anilino-4-morpholino-1,3,5-triazine-6-yl-amino)-stilbene-2,2'-disulphonic acid or similarly constructed compounds which, instead of the morpholino group, contain a diethanolamino group, a methylamino group or a 2-methoxyethylamino group, are suitable. Brighteners for polyamide fibres include those of the type of 1,3-diaryl-2-pyrazolines, for example the compound 1-(p-sulphamoylphenyl)-3-(p-chlorophenyl)-2-pyrazoline as well as similarly constructed compounds which contain, instead of the sulphamoyl group, for example the methoxycarbonyl-, 2-methoxyethoxycarbonyl-, acetyl-amino- or vinylsulphonyl group. Useful polyamide brighteners are also the substituted aminocoumarins, for example the 4-methyl-7-dimethylamino- or 4-methyl-7-diethylamino-coumarin. Further, the compounds 1-(2-benzimidazolyl)-2-(1-hydroxyethyl-2-benzimidazolyl)-ethylene and 1-ethyl-3-phenyl-7-diethylamino-carbostyril are useful as polyamide brighteners. The compounds 2,5-di-(2-benzoxazolyl)-thiophene, 2-(2-benzoxazolyl)-naphtho[2,3-b]-thiophene and 1,2-di (5-methyl-2-benzoxazolyl)-ethylene are suitable as brighteners for polyester and polyamide fibres. Furthermore, brighteners of the type of the substituted 4,4'-distyryl-diphenyl may be present; for example the compound 4,4'-bis(4-chloro-3-sulphostyryl)-diphenyl. Mixtures of the above-mentioned brighteners may also be used.

Compositions according to the invention of pulverulent to granular character are of particular practical interest, and may be prepared by processes known in the art.

Thus, for example, the pulverulent aluminium silicates can be mixed in a simple way with the other components of the washing composition, while oily or pasty components as for example nonionics, are sprayed on the powder. Another possible preparation consists in the incorporation of the pulverulent aluminium silicates into an aqueous slurry of the other components of the composition, which

is then converted into a powder by crystallisation processes or by drying by heat to remove the water. After the hot drying, for example on rollers or in spray towers, components sensitive to heat and moisture can then be incorporated, as for example bleaching agents and activators for these, enzymes, antimicrobial substances and so on.

There is first of all described the preparation of the boron or aluminium silicate cation exchangers to be used in the compositions of the invention, for which no protection is claimed here.

An aqueous aluminate solution of the concentration defined in the following preparations I to XX is diluted with deionised water and was mixed with vigorous stirring with an aqueous silicate solution of the concentration defined in the following preparations I to XX in a vessel of 15 litres capacity. Both solutions were at room temperature. An X-ray amorphous sodium aluminium silicate was formed with an exothermic reaction, as the primary precipitated product. After 10 minutes vigorous stirring, the suspension of the precipitated product was transferred to a crystallisation vessel, where it remained for some time at elevated temperature as hereinafter defined in the following preparations I to XX for the purpose of crystallisation. After filtering off by suction the liquid from the crystal slurry and then washing with deionised water until the washings had a pH value of about 10, the filter residue was dried. If there is any deviation from this general method of preparation, this is expressly mentioned in the following preparations I to XX. Thus, for example, in some cases the crystal slurry was used for washing experiments. The water contents were determined by heating the products for an hour at 800°C.

In the preparation of microcrystalline aluminium silicates characterised by the addition "m" to the aluminium silicate in question, aluminate solution diluted with deionised water was mixed with the silicate solution and treated with a high-speed intensive stirrer (10,000 rpm; Product "Ultraturrax" of the firm Janke und Kundel IKA-Werk, Staufen/Breisgau/Federal Republic of Germany). After 10 minutes vigorous stirring the suspension of the amorphous precipitation product was transferred to a crystallisation vessel, where the formation of large crystals was prevented by stirring the suspension. After filtering off the liquor by suction from the crystal slurry and then washing with deionised water, until the washings has a pH value of about 10, the filter residue was dried, then ground in a ball mill and separated into two fractions in a centrifugal separator (Mikroplex-air separator of the firm Alpine, Augsberg, Federal Republic of Germany), of which the finer contained no parts above 10. The distribution of grain size was determined by means of a sedimentation balance.

The degree of crystallisation of an aluminium silicate can be determined from the intensity of the interference lines of an X-ray diffraction diagram of the respective product compared with the corresponding diagram of X-ray amorphous or fully crystalline products.

All percentage data are weights per cent.

The calcium binding capacity of the aluminium silicates was determined in the following way:

1 litre of an aqueous solution containing 0.594 g of $CaCl_2$ (=300 mg CaO/litre=30° German hardness) and ajusted to a pH value of 10 with dilute NaOH is mixed with 1 g of aluminium silicate (referred to AS). Then the suspension is vigorously stirred at a temperature of 22°C. (±2°C.) for 15 minutes. After filtering off the aluminium-silicate the residual hardness x in mg CaO/l of the filtrate is determined. Therefrom the calcium binding capacity is calculated in mg CaO/g AS according to the formula: 300—x.

If the calcium binding capacity is determined at higher temperatures, for example at 60°C., between values are found throughout than at 22°C. This circumstance distinguishes the aluminium silicates compared with most of the soluble complex-forming substances previously proposed for use in washing agents and in its use represents a particular technical advance.

Preparation conditions for the aluminium silicate I:

| | |
|---|---|
| Precipitation: | 2.985 kg aluminate solution of the composition: 17.7% $Na_2O$, 15.8% $Al_2O_3$, 66.5% $H_2O$.<br>0.15 kg sodium hydroxide<br>9.420 kg water<br>2.445 kg of a 25.8% sodium silicate solution (freshly prepared from a commercial waterglass and silicic acid easily soluble in alkali of the composition: 1 $Na_2O$, 6.0 $SiO_2$ |
| Crystallisation: | 24 hours at 80°C. |
| Drying: | 24 hours at 100°C. |
| Composition: | 0.9 $Na_2O$, 1 $Al_2O_3$, 2.04 $SiO_2$, 4.3 $H_2O$ (=21 .6% $H_2O$) |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 150 mg CaO/g AS |

When the product so obtained is dried for 1 hour at 400°C., an aluminium silicate Ia is obtained of the composition:

0.9 $Na_2O$, 1 $Al_2O_3$, 2.04 $SiO_2$, 2.0 $H_2O$ (=11.4% $H_2O$)

which is also suitable for the purposes of the invention.

Preparation conditions for aluminium silicate II:

| | |
|---|---|
| Precipitation: | 2.115 kg aluminate solution of the composition: 17.7% $Na_2O$, 15.8% $Al_2O_3$, 66.5% $H_2O$<br>0.585 kg sodium hydroxide<br>9.615 kg water<br>2.685 kg of a 25.8% sodium silicate solution of the composition 1 $Na_2O$, 6 $SiO_2$ (prepared as given under I) |
| Crystallisation: | 24 hours at 80°C. |
| Drying: | 24 hours at 100°C. and 20 Torr |
| Composition: | 0.8 $Na_2O$, 1 $Al_2O_3$, 2.665 $SiO_2$, 5.2 $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 120 mg CaO/g AS |

This product also can be dehydrated by further drying (1 hour at 400°C. to the composition:

0.8 $Na_2O$, 1 $Al_2O_3$, 2.65 $SiO_2$, 0.2 $H_2O$

this dehydrated product IIa is also useful for the purposes of the invention.

The aluminium silicates I and II show in the X-ray diffraction diagram the following interference lines:

d-values, absorbed with Cu—K$\alpha$-radiation in Å

| I | II |
|---|---|
| — | 14.4 |
| 12.4 | — |
| — | 8.8 |
| 8.6 | — |
| 7.0 | — |
| — | 4.4(+) |
| 4.1(+) | — |
| — | 3.8(+) |
| 3.68(+) | — |
| 3.38(+) | — |
| 3.26 | — |
| 2.96(+) | — |
| — | 2.88(+) |
| — | 2.79(+) |
| 2.73(+) | — |
| — | 2.66(+) |
| 2.60(+) | — |

It is entirely possible that in the X-ray diffraction diagram not all these interference lines appear, especially when the aluminium silicates are not completely crystallised. Therefore the most important d-values for the characterisation of these types were marked with a "(+)".

Preparation conditions for the aluminium silicate XII:

| | |
|---|---|
| Precipitation: | 2.01 kg aluminate solution of the composition: 20.0% $Na_2O$, 10.2% $Al_2O_3$, 69.8% $H_2O$<br>0.395 kg sodium hydroxide<br>10.405 kg water<br>2.19 kg of a 25.8% sodium silicate solution of the composition:<br>1 $Na_2O$, 6 $SiO_2$ (prepared as given under I) |
| Crystallisation: | 24 hours at 80°C. |
| Drying: | 24 hours at 100°C. |
| Composition: | 0.9 $Na_2O$, 1 $Al_2O_3$, 2 $SiO_2$, 3 $H_2O$ |
| Degree of crystallisation: | completely crystalline |
| Calcium binding capacity: | 160 mg CaO/g AS |

Preparation conditions for the aluminium silicate XIII:

| | |
|---|---|
| Precipitation: | 2.985 kg aluminate solution of the composition: 17.7% $Na_2O$, 15.8% $Al_2O_3$, 66.5% $H_2O$<br>0.150 kg sodium hydroxide<br>9.420 kg water<br>2.445 kg of a 25.8% sodium silicate solution of the composition:<br>1 $Na_2O$, 6 $SiO_2$ (prepared as given under I) |
| Crystallisation: | 24 hours at 80°C. |

For the preparation of the potassium aluminium silicate the liquor was filtered off by suction, the residue was washed with water and suspended in an aqueous solution containing KCl. After heating for 30 minutes at 80—90°C., the solid was filtered off and washed.

| | |
|---|---|
| Drying: | 24 hours at 100 °C. |
| Composition: | 0.28 $Na_2O$, 0.62 $K_2O$. 1 $Al_2O_3$, 2.04 $SiO_2$. 4.3 $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 170 mg CaO/g AS |

Preparation conditions for the aluminium silicate XV:

| | |
|---|---|
| Precipitation: | 8.450 kg aluminate solution of the composition: 11.3% $Na_2O$, 18.7% $Al_2O_3$, 70.0% $H_2O$ were directly mixed with 6.550 kg of a 34.9% sodium silicate solution of the composition:<br>1 $Na_2O$, 3.46 $SiO_2$ |
| Crystallisation: | 24 hours at 80°C. |
| Drying: | omitted |
| Composition: | 1.5 $Na_2O$, 1 $Al_2O_3$, 2 $SiO_2$, x $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 170 mg CaO/g AS |

Preparation conditions for the boron silicate XVI:

| | |
|---|---|
| Precipitation: | 3.20 kg borate solution of the composition: 19.7% $Na_2O$, 19.7% $B_2O_3$, 60.6% $H_2O$<br>9.55 kg water<br>2.25 kg of a 34.5% sodium silicate solution of the composition:<br>1 $Na_2O$, 3.46 $SiO_2$ |
| Crystallisation: | 24 hours at 80°C. |
| Drying: | 24 hours at 100°C. and 20 Torr |
| Composition: | 1.5 $Na_2O$, 1 $B_2O_3$, 2 $SiO_2$, 1.5 $H_2O$ |
| Degree of crystallisation: | chiefly crystalline |
| Calcium binding capacity: | 120 mg CaO/g AS |

The primary particle sizes of the aluminium or boron silicates I—XVI here described were in the range from 10 to 45 $\mu$.

Preparation conditions for the aluminium silicate Im:

| | |
|---|---|
| Precipitation: | as with aluminium silicate I |
| Crystallisation: | 6 hours at 90°C. |
| Drying: | 24 hours at 100°C. |
| Composition: | 0.9 $Na_2O$, 1 $Al_2O_3$, 2.04 $SiO_2$, 4.3 $H_2O$ (=21.6% $H_2O$) |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 170 mg CaO/g AS |

Preparation conditions for the aluminium silicate IIm:

| | |
|---|---|
| Precipitation: | as with aluminium silicate II |
| Crystallisation | 12 hours at 90°C. |
| Drying: | 24 hours at 100°C. and 20 Torr |
| Composition: | 0.8 $Na_2O$, 1 $Al_2O_3$, 2.655 $SiO_2$, 5.2 $H_2O$ |
| Degree of crystallisation | fully crystalline |
| Calcium binding capacity: | 145 mg CaO/g AS |

Preparation conditions for the aluminium silicate XIIm:

| | |
|---|---|
| Precipitation: | as with aluminium silicate XII |
| Crystallisation: | 6 hours at 90°C. |
| Drying: | 24 hours at 100°C. |
| Composition: | 0.9 $Na_2O$, 1 $Al_2O_3$, 2 $SiO_2$, 3 $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 175 mg CaO/g AS |

Preparation conditions for the aluminium silicate XIIIm:

| | |
|---|---|
| Precipitation: | as with aluminium silicate XIII |
| Crystallisation: | 6 hours at 90°C. |

For the preparation of the potassium-aluminium silicate the liquor was filtered off by suction, the residue was washed with water and suspended in an aqueous solution containing KCl. After heating for 10 minutes at 80—90°C., the solid was filtered off and washed.

| | |
|---|---|
| Drying: | 24 hours at 100°C. |
| Composition: | 0.28 $Na_2O$, 0.62 $K_2O$, 1 $Al_2O_3$, 2.04 $SiO_2$, 4.3 $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 180 mg CaO/g AS |

Preparation conditions for the aluminium silicate XVm:

| | |
|---|---|
| Precipitation: | as with aluminium silicate XV |
| Crystallisation: | 24 hours at 80°C. |
| Drying: | The filter cake was not dried, but after washing was suspended in water and used in this form for the technical application investigations. |
| Composition: | 0.9 $Na_2O$, 1 $Al_2O_3$, 2 $SiO_2$, x $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 170 mg CaO/g AS |

Preparation conditions for the aluminium silicate XVIIIm:

| | |
|---|---|
| Precipitation: | as with aluminium silicate XV |
| Crystallisation: | 6 hours at 90°C. |
| Drying: | 24 hours at 100°C. |
| Composition: | 0.9 $Na_2O$, 1 $Al_2O_3$, 2 $SiO_2$, 4.4 $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 172 mg CaO/g AS |

Preparation conditions for the aluminium silicate XIXm:

| | |
|---|---|
| Precipitation: | 2.96 kg aluminate solution of the composition: 17.7% $Na_2O$, 15.8% $Al_2O_3$, 66% $H_2O$<br>0.51 kg sodium hydroxide<br>8.45 kg water<br>3.00 kg of a commercial sodium silicate solution of the composition:<br>8.0% $Na_2O$, 26.9% $SiO_2$, 65.1% $H_2O$ |
| Crystallisation: | 12 hours at 90°C. |
| Drying: | 12 hours at 100°C. |
| Composition: | 0.93 $Na_2O$, 1 $Al_2O_3$, 2.75 $SiO_2$, 5.5 $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 125 mg CaO/g AS |

Preparation conditions for the aluminium silicate XXm:

| | |
|---|---|
| Precipitation: | 0.76 kg aluminate solution of the composition: 36.0% $Na_2O$, 59.0% $Al_2O_3$, 5.0% $H_2O$<br>0.94 sodium hydroxide<br>9.49 kg water<br>3.94 kg of a commercial sodium silicate solution of the composition:<br>8.0% $Na_2O$, 26.9% $SiO_2$, 65.1% $H_2O$ |
| Crystallisation: | 12 hours at 90°C. |
| Drying: | 12 hours at 100°C. |
| Composition: | 0.9 $Na_2O$, 1 $Al_2O_3$, 3.1 $SiO_2$, 5 $H_2O$ |
| Degree of crystallisation: | fully crystalline |
| Calcium binding capacity: | 110 mg CaO/g AS |

The distribution of particle sizes determined by sedimentation analysis of the above-described microcrystalline products Im—XIIIm and XVIIIm—XXm lay within the following range:

$>40\mu$= 0% Maximum particle size=3—6$\mu$

$>10\mu$=85—95%

$< 8\mu$=50—95%

The distribution of particle sizes of the product XVm lay within the following range:

$>40\mu$= 0% Maximum particle size=1—3$\mu$

$<10\mu$=100%

$<8\mu$=99%

The constituents in the form of salts contained in the washing compositions of the following Examples are present as sodium salts, provided it is not stated otherwise. This also applies to the precipitation retarding agents, which for the sake of simplicity are denoted by the name of the corresponding acids. The terms or abbreviations used have the following meanings:

"ABS" is the salt of an alkylbenzenesulphonic acid having 10 to 15, preferably 11 to 13 carbon atoms in the alkyl chain, and obtained by condensation of straight-chain olefines with benzene and sulphonation of the alkylbenzene thus formed.

"HPK-Sulphonate" is a sulphonate obtained from hydrogenated palm kernal fatty acid methyl esters by sulphonation with $SO_3$,

"OA+x EO" and "TA+x EO" are the products of addition of ethylene oxide (EO) to technical oleyl alcohol (OA) and tallow fatty alcohol (TA) (I.V.=0.5) respectively, while the figures given for x represent the molar amount of ethylene oxide added on to 1 mol of alcohol.

"NTA" and "EDTA" are the salts of nitrilotriacetic acid and ethylenediaminotetraacetic acid respectively,
"HEDP" is the salt of 1-hydroxyethane-1,1-diphosphonic acid,
"DMDP" is the salt of dimethylaminomethane-diphosphonic acid,
"CMC" is the salt of carboxymethylcellulose.

The washing actions obtained with aluminium silicates according to the invention were demonstrated by washing experiments on cloths from untreated and easy care (crease-resistant) cotton or on mixed fabrics of polyester and dressed cotton provided with a test soiling of soot, iron oxide, kaolin and skin fat (test fabric prepared by the Laundry Research Institute Krefeld).

The experiments were carried out with service water of 16° German hardness partly in the Launderometer, partly in a commercial 4-kg drum washing machine (25 litres of liquid). Each vessel in the Lauderometer was charged with 2 test cloths each of 2.1 g and 2 clean cloths of the same material also of 2.1 g. The drum washing machine was charged with 6 test cloths of 20 x 20 cm dimensions each and 3.8 kg of clean fabric of the same kind.

The aluminium silicate concentrations of the treatment baths—like the aluminium silicate contents of washing compositions—relate to the anhydrous constituent of the product (determined by dehydrating at 800°C. for one hour); this also applies to the crystal slurry.

The washing times indicated in the separate experiments relate to the period of treatment at the said temperature including the heating up times. Cold service water was used for the rinsing.

The washing of the cloths in the Launderometer follows a rinsing of these four times with service water, each of 30 seconds; in the case of the experiments carried out in a commercial washing machine the draining of the washing and rinsing operations was fixed by the automatic device of the washing programme, which was provided for the textile material washed in each case. After drying and ironing the textiles their remission value was measured in a photoelectric Photometer "Elrepho" of the firm Zeiss under the Filter 6 (maximum transparency at 461 nm). The test fabric used in the experiments had as received a remission value of about 43.

Example 1.

This example demonstrated the washing action of different aluminium silicates to be used according to the invention without addition of further effective washing components.

Operating conditions:
untreated cotton
10 g/litre aluminium silicate
Bath ratio 1:12
Washed for 30 minutes at 90°C. in the Launderometer

In each parallel experiment the removal of dirt with water without any further addition and with addition of 10 g/litre of tripolyphosphate was determined. The "Water and tripolyphosphate values" thus found, like the other values, can be seen from the following list:

| Addition | | Remission |
|---|---|---|
| No addition | | 42.4 |
| $Na_5P_3O_{10}$ | | 76.8 |
| Aluminium silicate | I | 68.0 |
| " " | II | 66.0 |
| " " | XV(+) | 69.4 |
| Boron silicate | XVI | 66.0 |

(+) This aluminium silicate was used as precipitate or crystal slurry, of course after removing supernatant aqueous solution be decanting.

Example 2.

For demonstration of the improvement of the washing action of aluminium silicate-containing washing composition of the following formulation to which is added various builders capable of forming complexes or precipitating calcium, as hereinafter defined:

| | |
|---|---|
| 5.3% ABS | 2.5% $Na_2O$, 3.3 $SiO_2$ |
| 2.0% TA+14 EO | 1.2% CMC |
| 2.8% soap $C_{12}$—$C_{22}$ | 1.7% $MgSiO_3$ |
| 0 and 4.2% Complex-forming and precipitation builder for calcium | 6.3 and 2.1% $Na_2SO_4$ |
| 45.0% Al silicate Ia | $H_2O$ |
| 22.1% perborate | |

Operating conditions: dressed cotton
9 g/litre washing agent
bath ratio: 1:12
washed in the Launderometer at 90°C. for 30 minutes

The results are obtainable from the following list:

| Complex-forming compound or precipitation agent for calcium (as Na salts) | Remission |
|---|---|
| no addition | 64.0 |
| oxalic acid | 68.0 |
| tartaric acid | 66.0 |
| citric acid | 68.5 |
| O-carboxymethyl-tartronic acid | 74.8 |
| O-carboxymethyl-methyltartronic acid | 75.7 |
| $Na_5P_3O_{10}$ | 71.0 |
| aianine | 68.9 |
| glutamic acid | 72.0 |
| nitrilotriacetic acid | 71.0 |
| ethylenediamino-tetraacetic acid | 67.5 |
| N,N-dimethylamino-methanediphosphonic acid | 71.0 |
| polyacrylic acid | 69.5 |
| polyhydroxy-polycarboxylic acid I(+) | 71.7 |
| polyhydroxy-polycarboxylic acid II(+) | 72.0 |

(+) These two specimen substances were prepared by polymerisation of acrolein and treatment of the polymer according to Cannizzaro in the presence of formaldehyde.

A remission value of 72.5 is obtained under the following washing conditions: the washing composition is of the above indicated formulation, but the complex-forming compound and precipitation means for calcium and the aluminium silicate are completely replaced by sodium tripolyphosphate.

Example 3.

This example shows the action of the stepwise replacement of the triphosphate contained in a washing composition by aluminium silicate. The composition of the washing composition lay within the scope of the following formulation:

| | |
|---|---|
| 5.3% ABS | 22.1% $NaBO_2$, $H_2O_2$, $3H_2O$ |
| 2.0% TA+14 EO | 2.5% $Na_2O$, 3.3 $SiO_2$ |
| 2.8% soap $C_{12}$—$C_{22}$ | 1.2% CMC |
| 4.2—33.4% $Na_5P_3O_{10}$ | 1.7% $MgSiO_3$ |
| 45—0.0% aluminium silicate Ia | 2.1% $Na_2SO_4$ |
| | Remainder water |

Experimental conditions: dressed cotton
9 g/litre washing agent
bath ratio: 1:12
30 minutes at 90°C in the Launderometer

Washing result: see Table

| % content of $Na_5P_3O_{10}$ | Aluminium silicate | % Remission |
|---|---|---|
| 4.2 | 45.0 | 72 |
| 8.3 | 39.4 | 72 |
| 12.5 | 33.8 | 73 |
| 16.7 | 28.1 | 73 |
| 20.8 | 22.5 | 73 |
| 25.0 | 16.9 | 73 |
| 29.2 | 11.3 | 73 |
| 33.4 | 0 | 72 |

Examples 4 and 5.

These examples show the washing action of two washing compositions according to the invention on different textiles, compared with washing compositions in which the aluminium silicate is replaced by $Na_5P_3O_{10}$. The washing compositions had the following composition, while the washing composition according to the invention is in each case characterised by the addition "e", and the washing composition for comparison is characterised by the addition "v".

| Components of the washing composition | % wt. component in the case of component | | | |
|---|---|---|---|---|
| | 4v | 4e | 5v | 5e |
| ABS | 8.0 | 8.0 | — | — |
| TA+14 EO | 3.0 | 3.0 | — | — |
| OA+10 EO | — | — | 15.0 | 15.0 |
| Soap $C_{18}C_{22}$ | 3.5 | 3.5 | 3.0 | 3.0 |
| $Na_5P_3O_{10}$ | 33.4 | 2.5 | 10.0 | 3.0 |
| Aluminium silicate Ia | — | 45.0 | — | 27.0 |
| $NaBO_2$, $H_2O_2$, $3H_2O$ | 22.1 | 22.1 | 24.0 | 24.0 |
| $Na_2O$, 3.3 $SiO_2$ | 2.5 | 2.5 | 10.0 | 10.0 |
| CMC | 1.2 | 1.2 | — | — |
| $MgSiO_3$ | 1.7 | 1.7 | — | — |
| $Na_2SO_4$ | 19.0 | 2.1 | 30.0 | 10.0 |
| $H_2O$ | 5.6 | 8.4 | 8.0 | 8.0 |

Washing conditions: untreated and dressed cotton, cotton-polyester mixed fabric
Washing composition 4v and 4e: 9 g/litre
Washing composition 5v and 5e: 7.5 g/litre
Bath ratio: 1:5
Drum washing machine with the washing programme for boiling, washing,
Maximum temperature 95°C.
Washing result: see Table

| Washing agent according to Example | Remission of the washed fabric in % | | |
|---|---|---|---|
| | untreated cotton | dressed cotton | cotton-polyester |
| 4v | 83 | 74 | 70 |
| 4e | 82 | 73 | 74 |
| 5v | 82 | 74 | 74 |
| 5e | 82 | 73 | 74 |

If it is desired to obtain the following washing results as with tripolyphosphate, it is advisable to select the concentrations of aluminium silicate in the washing liquor to be somewhat higher than the concentrations of triphosphate in the bath for comparison.

Example 6.

Washing compositions of the following formulations 6a and 6b are suitable for use in trade laundries:

| Constituent | Content in % in the washing agent | |
|---|---|---|
| | 6a | 6b |
| ABS | 1.4 | 1.4 |
| OA+10 EO | 7.6 | 7.6 |
| $Na_2CO_3$ | 18.3 | 18.3 |
| $Na_2SiO_3$ | 5.4 | 5.4 |
| Aluminium silicate XVIIIm | 18.3 | 33.4 |
| $Na_5P_3O_{10}$ | 16.7 | 5.8 |
| CMC | 0.8 | 0.8 |
| Brightener, $Na_2SO_4$ | 10.0 | 10.0 |
| $H_2O$ | 21.5 | 17.3 |

The $Na_5P_3O_{10}$ can be replaced in the washing composition 6a by a phosphorus-free organic complex-forming substance for calcium, in the washing agent 6b by HEDP or another phosphonate complex binding calcium, by a phosphorus-free complex-forming substance for calcium or by a calcium precipitation agent not forming complexes (for example oxalic acid, adipic acid or sebacic acid in the form of their water-soluble salts).

Using each of these washing compositions, normally dirty domestic washing was washed while keeping to the following conditions:

Type of machine: Washing spin-drying machine of 90 kg capacity, loaded with 75 kg of washing

Water: service water softened to 5° German hardness

1. First washing operation:
   25 g washing composition/kg dry washing
   Bath ratio: 1:4
   9 minutes at 60°C
2. Second washing operation:
   20 g washing composition/kg dry washing
   0.5 g active oxygen (as $H_2O_2$)/kg dry washing
   Bath ratio: 1:4
   12 minutes at 90°C.
3. Rinsing operations: 2 x with softened water, 2 x with unsoftened water

In both cases the washing result was completely satisfactory.

Example 7.

A washing composition intended for washing heavily soiled occupational clothing has the following composition:

18.0% OA+10 EO
60.0% $Na_2CO_3$
12.0% aluminium silicate IIm
5.5% O-carboxymethyl-tartronic acid (Na salt)
1.3% CMC
0.3% brightener
2.9% $H_2O$

Example 8.

Bleaching washing compositions, of which the product a is suitable as addition to washing baths in the trade laundries, and the product b is suitable as addition acting in the cold for the after-rinsing water, have the following composition:

| Component | % wt. component in the agent according to Example 8a | 8b |
|---|---|---|
| $Na_2BO_2$, $H_2O_2$, 3 $H_2O$ | 36.0 | 18.0 |
| Tetraacetyl-glycoluril | — | 18.0 |
| $MgSiO_3$ | 3.6 | 3.6 |
| Aluminium silicate Im | 31.5 | 31.5 |
| Sodium citrate | 7.2 | 7.2 |
| $Na_2CO_3$ | 15.0 | 15.0 |
| Brightener | 0.3 | 0.3 |
| Water | 6.4 | 6.4 |

The formulations for further, aluminium silicate-containing washing compositions are given below

| Washing formulation % wt. component | component in the washing formulation according to Example 9 | 10 | 11 | 12 |
|---|---|---|---|---|
| TA + 14 EO | 7.0 | 10.3 | 10.7 | 6.8 |
| Aluminium silicate XIIm | 52.1 | 47.2 | 51.2 | 64.2 |
| $Na_5P_3O_{10}$ | — | 5.1 | 3.2 | 6.2 |
| Sodium citrate | 7.3 | — | 2.1 | — |
| EDTA | 0.2 | 0.2 | 0.1 | 0.3 |
| $Na_2O$ . 3.3 $SiO_2$ | 1.7 | 6.3 | 3.1 | 3.5 |
| $NaBO_2$ . $H_2O_2$ . 3 $H_2O$ | 24.9 | 24.9 | 20.3 | — |
| CMC | 0.8 | 1.6 | 1.1 | 2.0 |
| $Na_2SO_4$ + $H_2O$ | 6.0 | 4.4 | 8.2 | 17.0 |

The formulations for further aluminium silicate-containing washing compositions are given below:

| Washing formulation % wt. component | Component in the washing formulation according to Example 13 | 14 | 15 | 16 |
|---|---|---|---|---|
| HPK-sulphonate | 1.0 | 2.6 | – | 1.6 |
| ABS | 4.5 | 4.7 | 7.1 | – |
| TA + 14 EO | 2.3 | 1.9 | – | 6.4 |
| OA + 10 EO | – | – | – | 4.1 |
| Soap | 2.0 | 1.6 | 3.2 | – |
| Aluminium silicate XVIII m | 45.0 | 47.3 | 48.1 | 49.3 |
| $Na_5P_3O_{10}$ | 5.0 | 6.3 | 8.0 | 7.2 |
| EDTA | 0.2 | 0.9 | 0.2 | 0.2 |
| $Na_2O \cdot 3.3\ SiO_2$ | 6.5 | 3.7 | 2.6 | 3.4 |
| $NaBO_2 \cdot H_2O_2 \cdot 3\ H_2O$ | 25.1 | 26.3 | 22.3 | 22.1 |
| CMC | 1.3 | 0.9 | 1.5 | 1.6 |
| $Na_2SO_4 + H_2O$ | 7.1 | 3.8 | 7.0 | 4.1 |

As may be seen from the Examples, especially from the experiments described therein, the aluminium silicates with cation-exchanging capacity to be used according to the invention are able to improve the washing power of a washing composition by binding the calcium present in the water and in the dirt, and to replace the tripolyphosphate partly or wholly. Provided formulations in the Examples still contain triphosphate, this can be replaced if necessary by phosphorus-free complex-forming substances; useful complex-forming compounds are found among the compounds in the Table of Example 2 (oxalic acid is not a complex-forming substance, but a precipitation agent).

Although the aluminium silicates are water-insoluble, they can also be well rinsed out of the washed textiles and they are not deposited in the washing machine or in the waste water conduits or sewers.

The experiments and compositions described in Examples 1 to 6 were carried out or prepared respectively also with use of microcrystalline aluminium silicates. It was thereby shown that the microcrystalline aluminium silicates had a better action when the products to be compared with one another have the same composition. Individually the following microcrystalline aluminium silicates were tested or used for the preparation of washing compositions or washing assistants:

In Example 1: aluminium silicates Im, IIm and IVm
In Example 2: aluminium silicate XIIm
In Example 3: aluminium silicate Im
In Example 4: aluminium silicate XIIIm
In Example 5: aluminium silicate XIIIm

The $Na_5P_3O_{10}$ can be replaced in washing formulation 6a by a phosphorus-free organic complex-forming compound for calcium, in washing formulation 6b by HEDP or another phosphate complex binding calcium, by a phosphorus-free complex-forming compound for calcium or by a non-complex-forming calcium precipitation means (for example oxalic acid, adipic acid or sebacic acid in the form of their water-soluble salts).

The washing formulations in the following Examples were prepared by use of aluminium silicates XIIm and XVIIIm:

| Washing formulations % wt. component | Component in washing formulation according to Example 17 | 18 | 19 | 20 |
|---|---|---|---|---|
| TA + 14 EO | 7.0 | 10.3 | 10.7 | 6.8 |
| Aluminium silicate XIXm | 50.1 | 45.2 | 49.2 | 62.2 |
| $Na_5P_3O_{10}$ | – | 5.1 | 3.2 | 6.2 |
| Sodium citrate | 7.3 | – | 2.1 | – |
| EDTA | 0.2 | 0.2 | 0.1 | 0.3 |
| $Na_2O$ . 3.3 $SiO_2$ | 1.7 | 6.3 | 3.1 | 3.5 |
| $NaBO_2$ . $H_2O_2$ . 3 $H_2O$ | 24.9 | 24.9 | 20.3 | – |
| CMC | 0.8 | 1.6 | 1.1 | 2.0 |
| $Na_2SO_4$ + $H_2O$ | 8.0 | 6.4 | 10.2 | 19.0 |

| Washing formulation % wt. component | Component in washing formulation according to Example 21 | 22 | 23 | 24 |
|---|---|---|---|---|
| HPK-sulphonate | 1.0 | 2.6 | | 1.6 |
| ABS | 4.5 | 4.7 | 7.1 | – |
| TA + 14 EO | 2.3 | 1.9 | – | 6.4 |
| OA + 10 EO | – | – | – | 4.1 |
| Soap | 2.0 | 1.6 | 3.2 | – |
| Aluminium silicate XXm | 43.0 | 45.3 | 46.1 | 45.3 |
| $Na_5P_3O_{10}$ | 5.0 | 6.3 | 8.0 | 7.2 |
| EDTA | 0.2 | 0.9 | 0.2 | 0.2 |
| $Na_2O$ . 3.3 $SiO_2$ | 6.5 | 3.7 | 2.6 | 3.4 |
| $NaBO_2$ . $H_2O_2$ . 3 $H_2O$ | 25.1 | 26.3 | 22.3 | 22.1 |
| CMC | 1.3 | 0.9 | 1.5 | 1.6 |
| $Na_2SO_4$ + $H_2O$ | 9.1 | 5.8 | 9.0 | 8.1 |

A better rinsing out of the microcrystalline aluminium silicates used according to the invention showed especially at the edges and corners of bed or pillow covers as well as on collars and cuffs of shirts.

WHAT WE CLAIM IS:—

1. A process for washing and/or bleaching textiles by treatment with an aqueous liquor which contains in suspension a water-insoluble, synthetically produced, finely-divided, crystalline aluminium or boron silicate cation exchanger containing bound water having a calcium binding capacity (as hereinbefore

defined) of at least 50 mg CaO/g of water-free active substance (=AS) of the general formula

$$(Cat_{2/n}O)x,\ Me_2O_3,\ (SiO_2)y$$

in which Cat represents a cation of valency n exchangeable with calcium, x is a number from 0.7 to 1.5, Me represents boron or aluminium and y is a number from 0.8 to 6.

2. A process as claimed in claim 1 in which y of the general formula in claim 1 is a number from 1.3 to 4.

3. A process as claimed in claim 1 or 2 in which the silicate cation exchanger as defined in claim 1 or 2 has one of the following sets of d-values (in A) which are determinable by an X-ray diffraction diagram:

| | | | | |
|---|---|---|---|---|
| 12.4 | 8.6 | 7.0 | 4.1 | 3.68 |
| 3.38 | 3.26 | 2.96 | 2.73 | 2.60 |

or

| | | | | |
|---|---|---|---|---|
| 14.4 | 8.8 | 4.4 | 3.8 | |
| 2.88 | 2.79 | 2.66. | | |

4. A process as claimed in claim 1, 2 or 3 in which the silicate cation exchanger has a calcium binding capacity of up to 200 mg CaO/g AS.

5. A process as claimed in any one of claims 1 to 4 in which the silicate cation exchanger has the formula

$$0.7—1.1\ (Cat_{2/n}O),\ Me_2O_3,\ 1.3—2.4\ SiO_2$$

and a calcium binding capacity of 100—200 mg CaO/G AS.

6. A process as claimed in any one of claims 1 to 4 in which the silicate cation exchanger has the formula

$$0.7—1.1\ Na_2O,\ Al_2O_3,\ 2.4—3.3\ SiO_2.$$

7. A process as claimed in any one of claims 1 to 6 in which the silicate cation exchanger contains as cation sodium, lithium, potassium, ammonium, magnesium or cations of water-soluble organic bases.

8. A process as claimed in any one of claims 1 to 6 in which the silicate cation exchanger has a primary particle size of 0.1 to 100.

9. A process as claimed in claim 8 in which the primary particle size of the silicate cation exchangers is from 1 to 50.

10. A process as claimed in any one of claims 1 to 9 in which the treating liquor also contains in solution an inorganic and/or organic builder substance known to be able to form complexes with and/or to precipitate calcium, said builder being a meta-or polyphosphate, a polycarboxylic acid, a hydroxy-carboxylic acid, an amino carboxylic acid, a carboxyalkyl ether, a polyanionic polymeric carboxylic acid or a phosphonic acid or a salt thereof.

11. A process as claimed in claim 10 in which said builder is used in a concentration of from 0.05 to 2 g/litre.

12. A process as claimed in any one of claims 1 to 11 in which the treating liquor further contains an anionic surfactant of the sulphonate or sulphate types, a zwitterionic surfactant, a non-ionic surfactant or a bleaching agent.

13. A process as claimed in any one of claims 1 to 11 in which the inorganic and/or organic phosphorus builders are present in such amounts that the phosphorus content of the treatment liquor does not exceed 0.6 g/litre.

14. A process as claimed in claim 13 in which the inorganic and/or organic phosphorus builders are present in such amounts that the phosphorus content of the treatment liquor does not exceed 0.3 g/litre.

15. A process as claimed in any one of claims 1 to 14 in which at least 80% of the silicate cation exchanger particles have a size of from 10 to 0.01.

16. A process as claimed in claim 15 in which at least 80% of the silicate cation exchanger particles have a size of from 8 to 0.1.

17. A washing and/or bleaching composition for carrying out the process as claimed in any one of claims 1 to 16 comprising a silicate cation exchanger as defined in any one of claims 1 to 9 and 15 and 16 and at least one compound with a washing and/or bleaching action.

18. A composition as claimed in claim 17 in which the silicate cation exchanger is present in an amount of from 5 to 95% by weight.

19. A composition as claimed in claim 17 or 18 in which the silicate cation exchanger is present in an amount of from 15 to 60% by weight.

20. A composition as claimed in claim 17, 18 or 19 comprising an anionic surfactant of the sulphonate or sulphate type, a zwitterionic surfactant or a non-ionic surfactant, a builder substance which can complex or precipitate calcium selected from meta-or polyphosphate, polycarboxylic acids, hydroxy carboxylic acids, aminocarboxylic acids, carboxyalkyl ethers, polyanionic polymeric carboxylic acids and polyphosphonic acids and salts-thereof, or a bleaching agent.

21. A composition as claimed in claim 20 in which the builder substance is present in an amount of from 2 to 15% by weight.

22. A composition as claimed in claim 20 or 21 in which the surfactant is present in an amount of from 2 to 40% by weight.

23. A composition as claimed in claim 20, 21 or 22 which contains 5 to 60% by weight of a builder substance.

24. A composition as claimed in any one of claims 20 to 23 in which the bleaching agent is an active oxygen compound present in an amount of from 10 to 40 by weight.

25. A composition as claimed in claim 22 which also contains a stabiliser and/or activator for the active oxygen compound.

26. A composition as claimed in any one of claims 17 to 25 having the following Formulation:—

(A) 5—30% by wt. of an anionic surfactant of the sulphonate or sulphate type and/or a non-ionic and/or zwitterionic surfactant.

(B) 5—70% by wt. of a silicate cation exchanger as defined in any one of claims 1 to 9 and 14 and 15 (with reference to AS)

(C) 2—45% by wt. of a builder which is a complex former and/or precipitating agent for calcium as defined in claim 18.

(D) 0—50% by wt. of an alkaline builder other than (C) above, and

(E) 0—50% by wt. of a bleaching agent and other conventional detergent additives.

27. A composition as claimed in any one of claims 16 to 26 having a content of organic and/or inorganic phosphorus compounds such that the total phosphorus content of the composition does not exceed 6% by weight.

28. A composition as claimed in claim 27 in which the total phosphorus content of the composition does not exceed 3% by weight.

29. A composition as claimed in any one of claims 17 to 28 which is in pulverulent or granular form.

30. A method of producing a composition as claimed in any one of claims 17 to 29 in which a pulverulent silicate cation exchanger as defined in any one of claims 1 to 9 is mixed with the remaining components of the composition.

31. A method of producing a composition as claimed in any one of claims 17 to 29 in which a pulverulent silicate cation exchanger as defined in any one of claims 1 to 9 is incorporated in an aqueous slurry of the other components of the composition which are stable to water and heat, this slurry being dried and the dried product mixed with components of the composition which are not stable to heat and moisture.

32. A process as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

33. A composition as claimed in claim 17 substantially as hereinbefore described with reference to any one of the Examples.

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PATENTS ACT, 1949

SPECIFICATION NO 1473201

In accordance with the Decision of the Superintending Examiner, acting for the Comptroller-General, dated 14 April 1981, this Specification has been amended under Section 14 in the following manner:

Page 24, line 19, *delete* any one of claims 1 to *insert* claim
Page 24, *delete* lines 23 to 25
Page 24, *for* claims 7 to 16 *read* 6 to 15
Page 24, lines 26 and 29, *for* 6 *read* 5
Page 24, line 30, *for* 100 *read* 100$\mu$
Page 24, line 31, *for* 8 *read* 7
Page 24, line 32, *for* 50 *read* 50$\mu$
Page 24, line 33, Page 25, lines 46 and 49, *for* 9 *read* 8
Page 24, line 39, *for* 10 *read* 9
Page 24, line 41, *for* 11 *read* 10
Page 24, line 44, *delete* any one of claims 1 to 11 *insert* claim 9 or 10
Page 24, line 47, *for* 13 *read* 12
Page 24, line 50, *for* 14 *read* 13
Page 24, line 51, *for* 0.01 *read* 0.01$\mu$
Page 24, line 52, *for* 15 *read* 14
Page 24, line 53, *for* 0.1 *read* 0.1$\mu$
Page 24, *after* line 53 *insert* 16. A process as claimed in any one of claims 2 to 4 in which the silicate cation exchanger has the formula $0.7-1.1\ Na_2O, Al_2O_3, >2.4-3.3\ SiO_2$.
Page 25, line 2, *for* 16 *read* 13
Page 25, line 3, *delete* 9 and 15 and 16 *insert* 8
Page 25, line 7, *delete* 17 or
Page 25, line 14, *for* polyphosphonic *read* phosphonic
Page 25, line 24, *for* 22 *read* 24
Page 25, line 26, *for* 17 *read* 21
Page 25, line 31, *delete* 9 and 14 and 15 *insert* 8
Page 25, line 33, *for* 18 *read* 20
Page 25, line 37, *for* 16 *read* 20
Page 25, *after* line 43 *insert* 30. A composition as claimed in any of claims 17 to 29 which comprises a silicate cation exchanger as defined in claim 14 or 15. 31. A composition as claimed in any of claims 17 to 29 which comprises a silicate cation exchanger as defined in claim 16
Page 25, *for* claims 30 and 31, 32 and 33 *read* 32 and 33, 36 and 37
Page 25, *after* line 52, *insert* 34. A method as claimed in claim 32 or claim 33 in which the silicate cation exchanger is as defined in claim 14 or claim 15. 35. A method as claimed in claim 32 or claim 33 in which the silicate cation exchanger is as defined in claim 16.

THE PATENT OFFICE
*6 October 1982*

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